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Final Report for NASA Grant NAGW-3117

Title: Ancient Sulfur Biogeochemistry

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Rational:

The sediment geochemical record is rich with indicators of environmental change over the course of Earth history. The challenge in understanding this record is first to collect information that has been minimally affected by post depositional processes, and second, to learn to faithfully interpret the information. This research has focused primarily on the interpretation of the ancient sulfur isotopic record as it pertains to the evolution of the sulfur cycle on Earth. The modern oceans are rich in dissolved sulfate, and sulfate reduction is a major process of sedimentary carbon oxidation. The accumulation of sulfate in ancient oceans was a major milestone in the evolution of the Earth surface environment. This is because sulfate is the largest reservoir of oxidized species on the Earth surface, and the significant accumulation of sulfate in seawater signalled the beginnings of modern-style carbon cycling.

The sulfide produced during sulfate reduction is depleted in the isotope ^{34}S , compared to the starting sulfate. This phenomena creates the basis for interpreting the ancient sulfur record.

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However, the range in possible fractionations during sulfate reduction, and environmental controls on the fractionation, is poorly known. Also, the complete suite of factors other than sulfate reduction by which modern sediments acquire their sulfur isotopic signature is not known. This is demonstrated by noting that pure cultures of sulfate reducing bacteria cannot produce the isotopic composition of sulfide in modern marine sediments (Fig. 1). Our goals have been: 1) to understand the controls on the isotopic composition of sulfide in modern marine sediments, and to apply this understanding to ancient sediments; 2) to better define the history of sedimentary sulfur, allowing us to better understand how this history speaks to environmental change; 3) to explore case-studies of sediment diagenesis in ancient sediments to compliment the isotopic record. We have made significant progress in all of these areas.

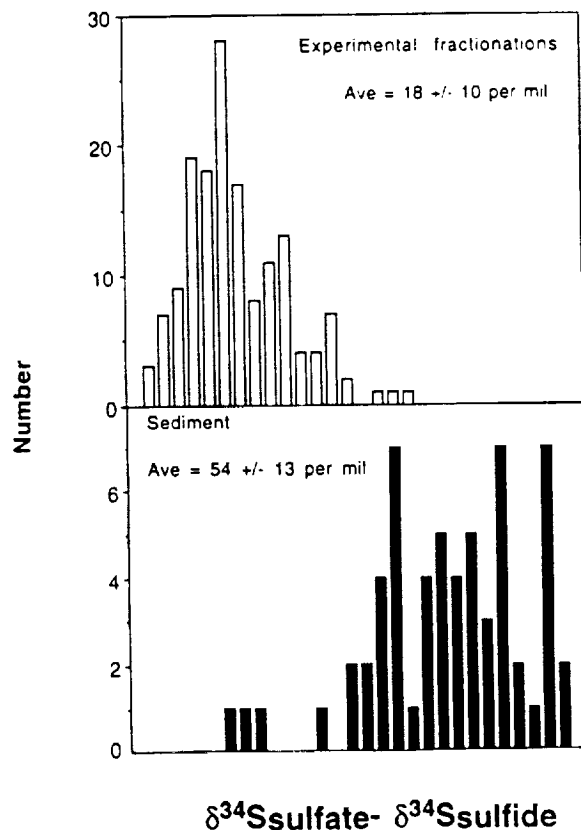
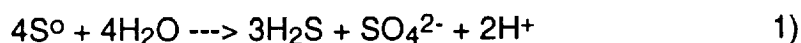


Fig 1. Isotopic fractionation during sulfate reduction for pure cultures of sulfate reducing bacteria (open bars), compared to isotopic composition of sulfide in marine sediments (Closed bars).

Modern Sediment studies:

To explore the dilemma posed in Fig. 1, we have explored the isotopic consequences of the oxidative part of the sedimentary S-cycle. Our interest in this part of the S-cycle is spurred by the fact that most of the sulfide produced by sulfate reduction in sediments is reoxidized and lost from the sediment. We have first documented that elemental sulfur is an important intermediate in sulfide oxidation, and that the most likely fate of elemental sulfur is disproportionation (Eqn. 1; Canfield and Thamdrup, in press).



We have documented that elemental sulfur disproportionation is an autotrophic, bacterial process, conducted by a range of microorganisms. We are presently exploring the diversity of this bacterial population. Further, we have discovered that accompanying the disproportionation, there is an isotopic fractionation such that the sulfide is isotopically depleted in ^{34}S , and the sulfate is isotopically enriched in ^{34}S compared to the elemental sulfur (Fig. 2). Hence, with continued cycles of sulfide oxidation to elemental sulfur, and disproportionation, we can generate the isotopically light (^{34}S -depleted) sulfides in Fig. 1.

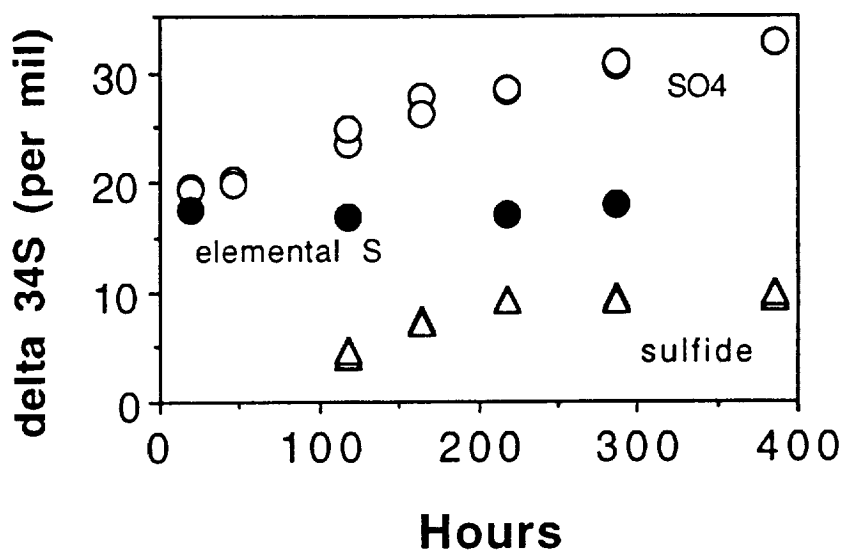


Fig. 2. The isotopic composition of sulfur species are shown in duplicate time course experiments on elemental sulfur-amended sediment undergoing active elemental sulfur disproportionation.

This is a major finding as it allows us for the first time to understand the isotopic composition of marine sedimentary sulfides, and provides an important basis for interpreting the sulfur isotope record through the Cambrian-Precambrian boundary (see below). These findings have been summarized in Canfield and Thamdrup (1994).

Previous workers have suggested that sulfate reduction has been an active process in marine sediments since 3.5 bybp. It is clear that little fractionation is observed in marine sedimentary sulfides from 3.5 bybp until about 2.2 bybp. However, these authors have argued sulfate reduction has taken place at very rapid rates in an ancient-warm ocean. The rationale is that at high rates of sulfate reduction, the demand for sulfate by an organism may be so high that no or little fractionation will occur, similar to the carbon fractionation during photosynthesis. We tested this model by exploring fractionation in microbial mats from Solar Lake, Sinai. Microbial mats support the highest rates of sulfate reduction on the modern Earth and provide an excellent environment to test the influence of rate on fractionation. Our results demonstrate that at different temperatures (to induce different rates, rate data not shown) and at different concentrations of sulfate (between seawater to 3 times seawater) relatively high fractionations of between 18 to 35 per mil were observed. (Fig. 3). Hence, rapid rates of sulfate reduction do support isotopic fractionation, and the ancient isotopic record between 2.2 and 3.5 bybp is consistent with limited rather than significant sulfate reduction in the ocean. Also note that sulfate reduction alone does not give enough fractionation to explain the isotopic composition of the sedimentary sulfides, consistent with discussion above. These results are presently being prepared for publication.

Additional studies on modern sediments have documented the significance of sulfate reduction on carbon oxidation in modern coastal sediments (Canfield et al., 1993a,b). Significantly, we have also for the first time documented the importance of Fe-oxides as an electron acceptor in carbon mineralization. The large importance of Fe-oxides in modern environments gives us an indication that Fe-reduction may have been a very significant process of carbon mineralization in ancient Fe-oxide-rich sediments deposited as Banded Iron Formations (BIF's). In a pair of papers (Van Cappellen and Canfield, 1993; Canfield, 1994) we have explored the relationship between the presence and absence of oxygen on the efficiency of

carbon preservation in sediments. Since the burial and preservation of carbon in sediments liberates oxygen to the atmosphere, an understanding of the factors influencing preservation is crucial to understanding the progressive oxidation of the Earth's surface environment. Also, we have explored the reaction kinetics of sulfide with Fe minerals, allowing us to use Fe mineralogy as an indicator of ancient depositional environments, and to explore if extensive periods of sulfidic waters persisted in the past (Canfield et al., 1992; Raiswell and Canfield, submitted). Finally, we have presented a model for the deposition of Fe in the modern euxinic Black Sea which shows that modern and ancient euxinic basins have a more similar Fe cycle than previously appreciated (Canfield et al, submitted).

^{34}S Seawater- ^{34}S sulfide

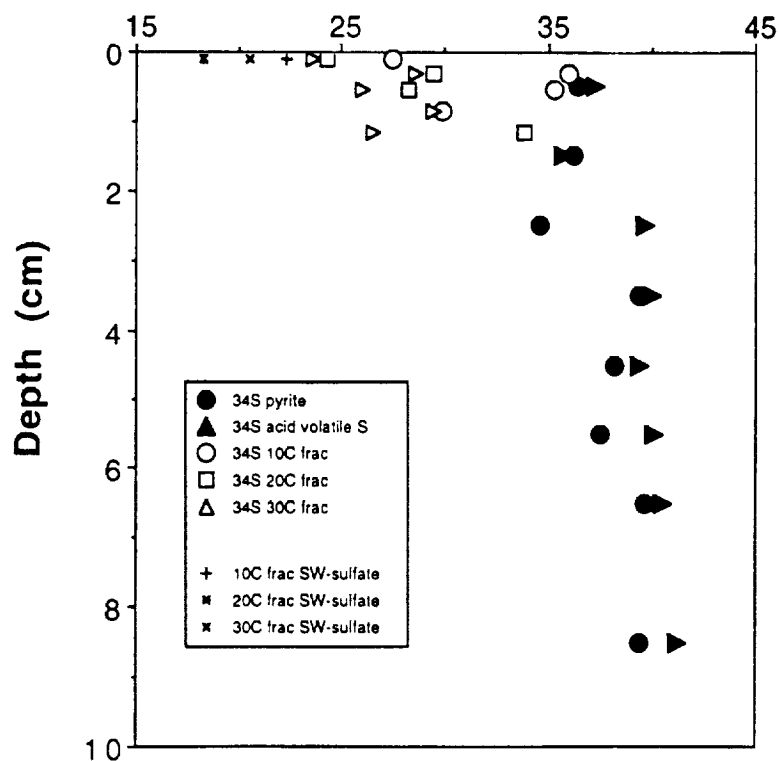


Fig. 3 The isotopic composition of reduced sulfur species in Solar Lake mats, compared to the fractionations measured during sulfate reduction by natural populations of sulfate reducing bacteria.

Sulfur Isotopic Record:

We have conducted an extensive literature survey of sedimentary sulfur isotopic compositions from present through the Mesoproterozoic (1.6 bybp). In compiling the data, no sediment that has experienced any documented hydrothermal input has been used. Also, sediment with high degrees of metamorphism have also been excluded. The record (Fig. 4), shows the isotopic composition of sulfides, the isotopic composition of sulfate over time (open band), and the isotopic composition of sulfate displaced by 55 per mil. Key points include a consistent offset between seawater sulfate and most depleted sulfides from present to about 650 mybp. As discussed above (Fig. 2) an offset of this magnitude requires an initial fractionation by sulfate reduction (20-30 per mil), modified substantially by disproportionation during sulfide oxidation (variable from 0 to about 40 per mil). Before about 650 mybp, fractionations are reduced, and maximum displacements in seawater sulfate are 20 to 30 per mil, consistent with fractionation during sulfate reduction without modification by the oxidative S-cycle. We conclude that between about 750 to 650 mybp conditions became conducive to the operation of the oxidative S-cycle. The most likely way this could happen is if oxygen became more available. Thus, we believe that we see in the S-isotope record between, 750 and 650 my ago, the first direct indication of the rise in atmospheric O₂ that preceded the evolution of the Metazoans.

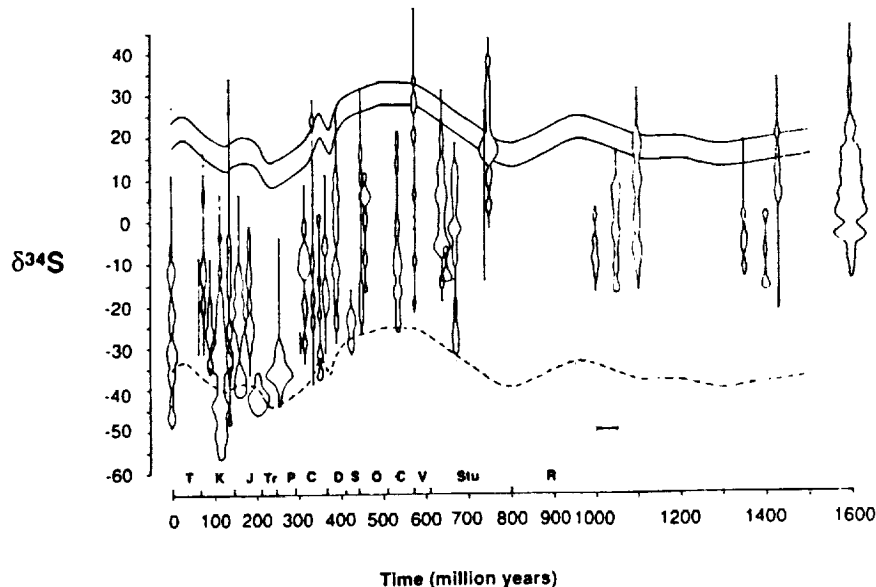


Fig. 4. Isotopic composition of sedimentary sulfide. See text for details.

We have further indications for the rise of atmospheric O₂ from the molecular phylogeny of sulfide oxidizing gradient bacteria that require O₂ for their metabolism. An internally calibrated molecular clock puts their evolution at about the same time. These results are currently being prepared for publication.

Site Studies:

We have travelled to the McRae shale in Western Australia. This shale was deposited about 2.5 bybp and we wish to explore the extent to which sulfate reduction dominated sediment diagenesis at this time. Our goal is to apply sediment analysis in addition to sulfur isotopic examination to evaluate the importance of sulfate reduction. Results are still preliminary, but sulfur isotopic compositions range from 0 to +15 per mil, indicative of, perhaps some sulfate reduction. Isotopic fractionations are, however, also consistent with modification by post-depositional S mobilization.

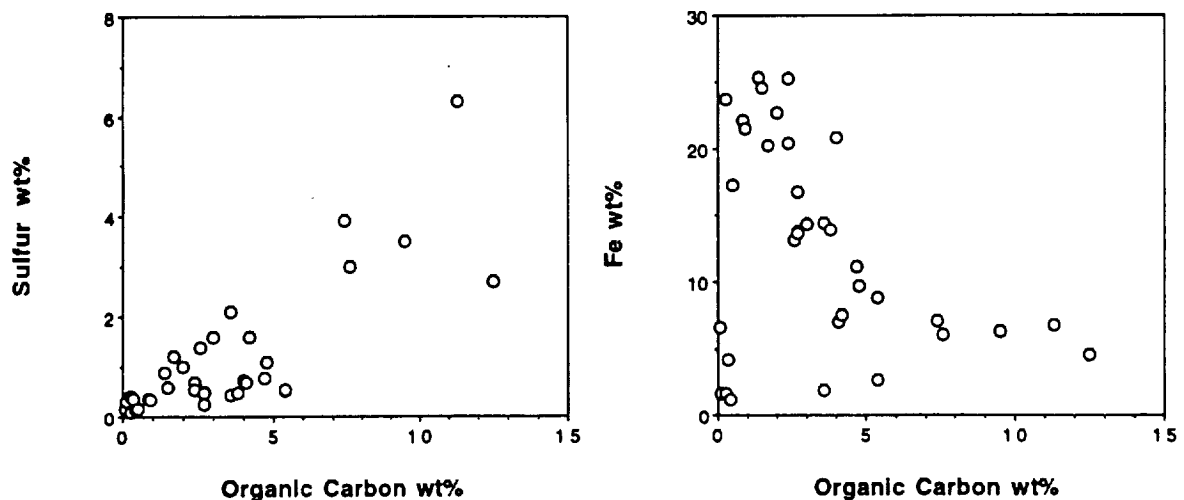


Fig. 5. Fe, sulfur, and organic carbon results from McRae shale sediments, Western Australia.

More informative is obtained from the sediment geochemical analysis. (Fig. 5). Here, we find that the concentration of organic carbon tracks that of sulfur. This means that sulfur is buried with carbon, as occurs in modern sediments supporting sulfate reduction. Hence, sulfate reduction is indicated. However, far more Fe oxides deposit in the sediment than are preserved as sulfide (Fig. 5; sulfur vs organic carbon would look like Fe vs organic carbon if all Fe was pyritized). In modern euxinic basins roughly 10 times more sulfide is produced than Fe deposits into the basin. Hence all Fe oxides are reacted with sulfide, and most of the sulfide is reoxidized back to sulfate at the chemocline. The predominance of Fe in McRae shale sediments, and during the time of BIF formation in general, requires that sulfate reduction must have been far less important than today. Otherwise all Fe oxides would have been reacted to form pyrite. Work on the McRae shale, and Fe mass balances for Precambrian oceans is still in progress.

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